

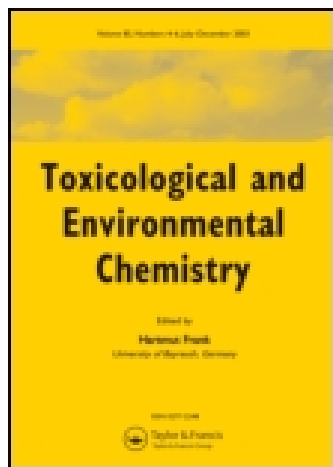
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Phototransformation of resorcinol induced by excitation of nitrite and nitrate ions. I: Nitrite ions

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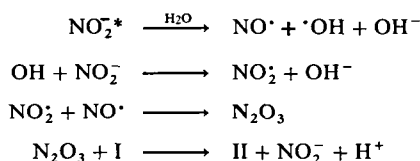
PHOTOTRANSFORMATION OF RESORCINOL INDUCED BY EXCITATION OF NITRITE AND NITRATE IONS. I: NITRITE IONS

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The excitation of nitrite ions in the presence of resorcinol (I) leads to the formation of 4-nitrosoresorcinol (II) as the major photoproduct. The reaction is inhibited by formate ions, but this inhibition is much more efficient in degassed solution than in air-saturated medium. In the absence of formate ions, the transformation is not affected by the presence of oxygen. From the influence of oxygen and formate ions, it is concluded that the formation of II results from a reaction of I with N_2O_3 . Dinitrogen trioxide is formed by oxidation of nitrite ions by hydroxyl radicals resulting from the photolysis of nitrite ions:



KEY WORDS: Photoreactions, phenolic compounds, resorcinol, nitrite ions

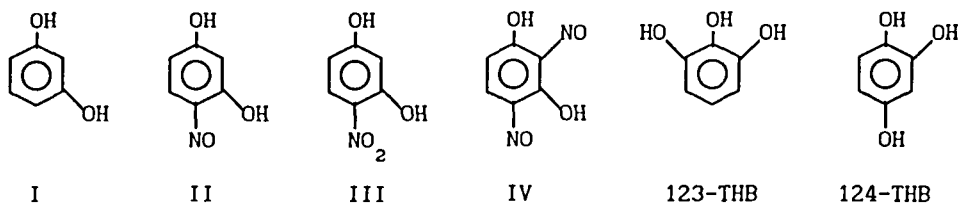
1 INTRODUCTION

Nitrate ions are often present in natural water. Their excitation in sunlight (maximum absorption at 302 nm) leads to the formation of nitrite ions and hydroxyl radicals¹. Nitrite ions absorb a larger part of solar energy than nitrate ions since their molar extinction coefficient at 352 nm is about three times higher than that of nitrate ions at 302 nm. Their photolysis leads also to the formation of hydroxyl radicals. Thus the excitation of nitrite and nitrate ions have a depolluting influence since hydroxyl radicals are able to oxidize most of the organic pollutants present in the aquatic medium²⁻⁴. But it was previously observed that the irradiation of aqueous solutions containing organic compounds and nitrite or nitrate ions also leads to the formation of nitroso or nitro-derivatives⁵⁻⁸ and in some cases, the formation of mutagens was observed^{9,10}. With aromatic compounds, the orientation of the reaction depends on the substitution on the ring since only hydroxylations were observed with chlorophenols and nitrophenols^{11,12}, whereas nitration and nitrosation compete with oxidation in the case of phenol⁷.

It is, therefore, important to study the mechanisms of the reactions involved and to determine the influence of various parameters such as pH, concentration and substitution of the ring (in the case of aromatic substrates) on the orientation of the reaction. It is commonly admitted that the oxidations involve hydroxyl radicals, but till now the mechanisms of photonitrations and photonitrosations have not been elucidated.

The reactions induced by excitation of nitrite ions are first considered because they are less complex than the reactions induced by nitrate ions in which they are involved as secondary reactions. The knowledge of reactions induced by nitrite ions is thus useful to understand the reactions induced by nitrate ions which will be studied later on. Resorcinol was chosen as the substrate because it has many industrial applications, and its induced phototransformation by nitrate or nitrite ions involve several pathways, as it was previously observed with phenol. The aim of the present work is to analyse the photoproducts formed in the induced phototransformation and to determine the influence of oxygen, nitrogen oxides, pH and hydroxyl radicals quenchers to contribute to a better understanding of the reactions involved.

Notations



2 EXPERIMENTAL DETAILS

2.1 Chemicals

Resorcinol (I) was provided by Merck (pro analysi grade >99%) and used without further purification.

4-nitrosoresorcinol (II) was obtained from the reaction of resorcinol with isopentyl nitrite according to¹³.

2,4-dinitrosoresorcinol (III) was prepared from reaction of resorcinol with sodium nitrite (1:2 mol/mol). It was controlled by mass spectrometry ($m/z = 168$) and NMR δ ppm 6.58 [9] and 8.08 [d]).

2.2 Irradiations

For analytical or preparative purposes, solutions were irradiated in polychromatic light using Duke Sun Lamps (20 W). The reactor was in pyrex to limit the irradiation range to 300–340 nm. In these conditions, the direct phototransformation of re-

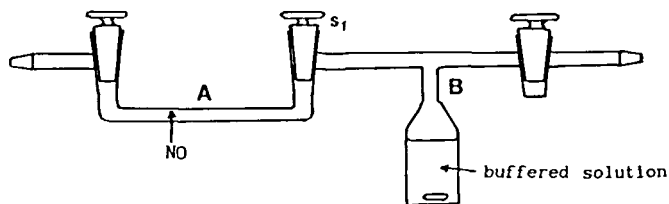


Figure 1 Device used to study the influence of NO^{\bullet} on resorcinol.

sorcinol was negligible compared to the induced phototransformation. For determinations of quantum yields solutions were irradiated in monochromatic parallel beam at 313 or 366 nm.

The incident photon flow was evaluated using potassium ferrioxalate as actinometer. The values obtained were 1.9×10^{15} and 0.43×10^{15} photons $\text{cm}^{-2} \cdot \text{s}^{-1}$ at 366 nm and at 313 nm respectively.

UV spectra were recorded on CARY 118C or CARY 3 instruments.

In most of the cases, specially for mass balances, solutions were buffered between $\text{pH} = 7.0$ and $\text{pH} = 7.5$ with phosphates, to eliminate the influence of nitrous acid ($\text{pK}_a = 3.37$).

2.3 Analyses

HPLC analyses were carried out on Beckman chromatograph (UV detection) or on Waters chromatograph equipped with a photodiode array detector. In any case, a classical C_{18} (250×4 mm) column was used.

2.4 Reaction of resorcinol with nitrogen monoxide

A special device was used to study the behaviour of resorcinol in the presence of NO^{\bullet} (Figure 1).

The part A was filled with NO^{\bullet} gas provided by the company Alpha Gaz. A solution of resorcinol ($\text{pH} = 7.2$) was introduced and deoxygenated in the part B. The stopcock S_1 was opened and the solution was stirred during 48 hours. The unreacted NO^{\bullet} was eliminated by argon flow and the solution was analysed by HPLC.

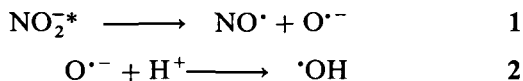
3 PHOTOCHEMICAL PROPERTIES OF NITRITE IONS

The maximum of the UV absorption band of NO_2^- is located at 352 nm and the corresponding molecular extinction coefficient was evaluated to be $22 \text{ M}^{-1} \cdot \text{cm}^{-1}$.

Table 1 Quantum yield of photolysis of NO_2^- at various wavelengths

λ (nm)	Φ	Ref.	λ (nm)	Φ	Ref.
298.5	0.07 ± 0.01	16	254	0.11 ± 0.01	12
337.1	0.07 ± 0.01	16	296	0.07 ± 0.01	12
354.6	0.025 ± 0.005	16	313	0.07 ± 0.01	12
371.1	0.015 ± 0.005	16	334	0.050 ± 0.008	12
308	0.07 ± 0.01	17	365	0.020 ± 0.005	12
351	0.046 ± 0.009	17			

It is well known that the excitation of nitrite ions in aqueous solution leads to the formation of hydroxyl radicals and nitrogen monoxide^{14,15}.



It was independently shown by several teams that the quantum yield of the photolysis ϕ increases with decreasing wavelengths as it appears in Table 1.

This wavelength effect was attributed to the existence of two $n \rightarrow \pi^*$ bands and one $\pi \rightarrow \pi^*$ band in the UV spectrum¹⁶. This phenomenon does not appear with nitrous acid ($\text{pK}_a = 3.37$). Its quantum yield of phototransformation is independent of the wavelength in the range 254–366 nm ($\Phi = 0.45 \pm 0.10$)¹².

4 RESULTS

4.1 Dark reactions

4.1a Nitrous acid

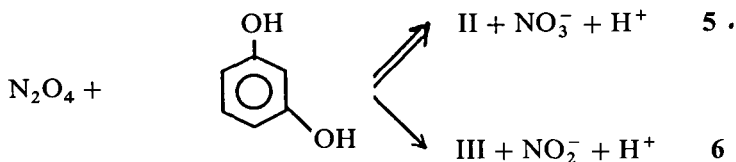
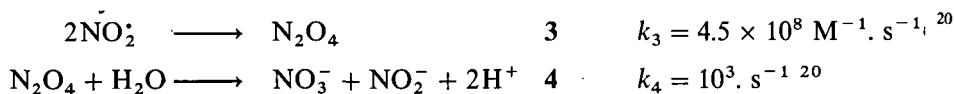
No reaction was observed in a solution of resorcinol (5×10^{-4} M) and nitrite ions (10^{-3} M) buffered at $\text{pH} = 7.1$, kept in the dark during 4 hours. In contrast at $\text{pH} = 3.2$, nitrosation occurs: 43% of resorcinol was converted after one hour.

In the induced phototransformation of resorcinol in air-saturated solution, no formation of trihydroxybenzene (THB) was observed, and only small amounts of 123-THB were detected in deoxygenated solution. To determine if this phenomenon can be attributed to an oxidation of THBs, their stabilities were controlled in our experimental conditions, i.e. at $\text{pH} = 7.3$ and in the presence of nitrite ions (10^{-3} M). In air-saturated medium, a solution of 124-THB 10^{-3} M was 57% transformed in 45 minutes and a solution of 123-THB 10^{-3} M was 15% transformed in 70 minutes. In deoxygenated solution, 124-THB was 9% transformed whereas the solution of 123-THB was unchanged after 70 minutes. Thus the oxidation of THBs can explain their absence only in aerated solutions.

4.1b Nitrogen oxides

The device described in Section 2.4 was used to study the behaviour of I with NO^{\bullet} . Only low percentages of I and NO^{\bullet} were consumed after 48 hours. Small amounts of II and traces of nitroresorcinol (III) were formed. It was concluded that pure NO^{\bullet} does not react with resorcinol. The limited reaction observed was attributed to traces of NO_2^{\bullet} contained in NO^{\bullet} (or residual traces of oxygen in the reactor).

To study the reaction of NO_2^{\bullet} , about 1 ml of NO_2^{\bullet} (gas) was injected in a solution of resorcinol 5×10^{-3} M (10 ml) buffered at $\text{pH} \approx 7.2$. The formation of II and 2,4-dinitrosoresorcinol (IV) was observed by HPLC analysis. III was also identified, but no formation of 123-THB or 124-THB was observed. The nitrosation and nitration are attributed to reactions of N_2O_4 that compete with its disproportionation into nitrite and nitrate ions.



A minor reaction of nitrous acid cannot be excluded because of the inhomogeneity of the pH during the dissolution of NO_2^{\bullet} .

4.2 Analytical and kinetic study of the induced phototransformation

Air saturated solutions of resorcinol (5×10^{-4} M) and sodium nitrite (5×10^{-4} – 5×10^{-3} M) buffered at $\text{pH} = 7.2$ – 7.3 were irradiated in the range 300–366 nm. In any case, the only primary photoproduct detected was 4-nitrosoresorcinol (II), but a minor formation of 2,4-dinitrosoresorcinol (IV) was also observed when the conversion rate overpassed c.a. 20%. The formation was attributed to a secondary reaction of II. Formation of 123-THB and 124-THB was not observed as it was in the phototransformation induced by excitation of nitrate ions¹⁸. The quantum yields of phototransformation of resorcinol (I) and of formation of II were evaluated by irradiating in monochromatic parallel beam at 366 and 313 nm for several concentrations of nitrite ions. It appears in Table 2 that the quantum yield of conversion of resorcinol is not significantly affected by the concentration of nitrite ions, but the formation of II is more selective with increasing concentration of nitrite ions. This effect will be discussed later on.

Solutions of same concentrations were deoxygenated and irradiated in the same conditions. No influence of oxygen was observed for $\text{NO}_2^- = 5 \times 10^{-3}$. With $\text{NO}_2^- = 5 \times 10^{-4}$, the quantum yield was only slightly reduced by deoxygenation.

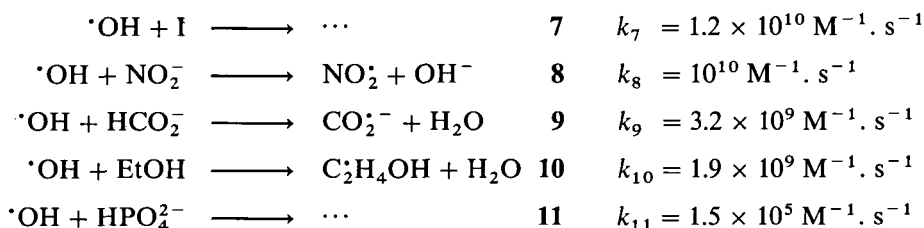
Table 2 Quantum yields of induced phototransformation of resorcinol and formation of 4-nitrosoresorcinol (II) at 366 nm evaluated by HPLC at 10% of conversion, in air saturated solution

$[NO_2^-]$	$\Phi_{\text{disp}} \times 10^{-2}$	Yield of II	$\Phi_{\text{form of II}} \times 10^{-2}$
$5 \times 10^{-4} \text{ M}$	1.21 ± 0.15	0.44	0.53 ± 0.07
$10 \times 10^{-4} \text{ M}$	1.15 ± 0.15	0.65	0.75 ± 0.09
$50 \times 10^{-4} \text{ M}$	1.05 ± 0.15	0.89	0.93 ± 0.13

Besides, a significant wavelength effect was observed by comparison of the quantum yields of phototransformation obtained at 366 and at 313 nm: the transformation was about twice as fast at 313 nm as at 366 nm. This effect is in good agreement with the wavelength effect observed in the photolysis of NO_2^- (Table 1).

4.3 Influence of formate ions

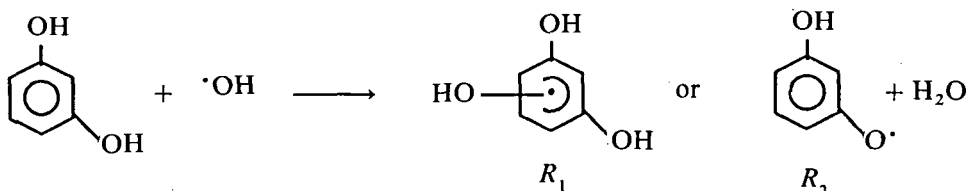
Formate ions and ethanol were used as $\cdot OH$ quenchers to determine the influence of hydroxyl radicals on the formation of nitrosoresorcinol, since formate ions can compete the reactions of nitrite ions and resorcinol with these radicals. The reaction of $\cdot OH$ with phosphate ions (0.013 M) used to buffer the solution can be neglected.



From the values of rate constants given in literature¹⁹, the quenching of $\cdot OH$ radicals by formate ions $5 \times 10^{-2} \text{ M}$ and by EtOH 0.17 M can be evaluated to be 91% and 95% respectively. The kinetic evolutions in the presence of formate ions and in the absence of $\cdot OH$ quencher are compared in Figure 2. It appears in Table 3 that formate ions have much more influence on the formation of product II in deoxygenated solution than in air-saturated medium.

5 DISCUSSION AND MECHANISM

It could be expected that 4-nitrosoresorcinol is formed by reaction of $NO\cdot$ with a radical resulting from the oxidation of resorcinol by hydroxyl radicals according to:



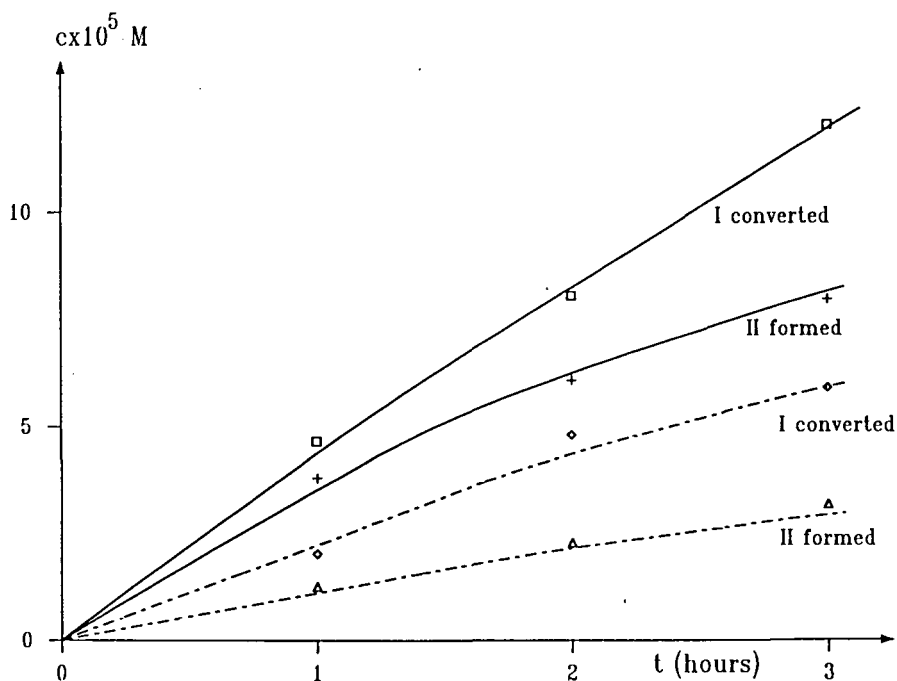
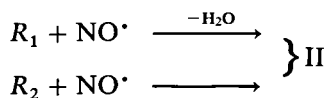


Figure 2 Kinetic study of a solution of resorcinol (5×10^{-4} M) and sodium nitrite (10^{-3} M) buffered at pH = 7.3, irradiated in the absence of formate ions (—) and in the presence of formate ions 5×10^{-2} M (---).



But this mechanism can be ruled out for several reasons:

i) In the absence of OH^\bullet quencher, the formation of II is only slightly affected by oxygen. Thus it might be admitted that the oxidations of R_1 and R_2 do not compete with their reaction with NO^\bullet .

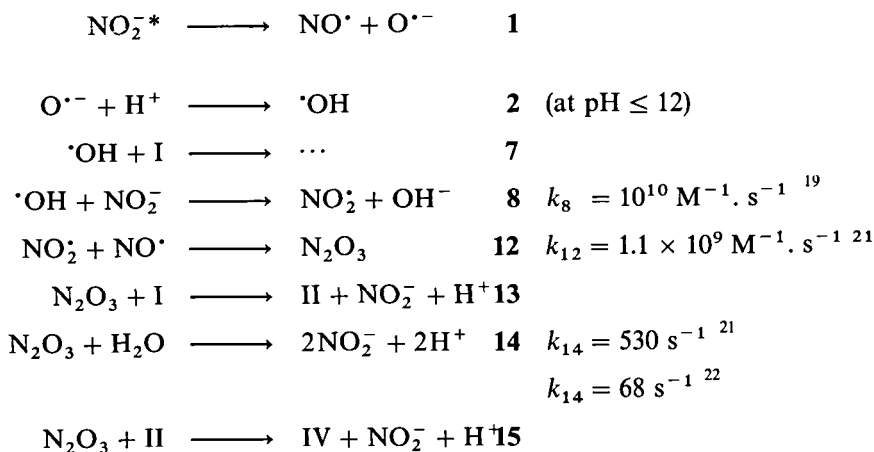
ii) In air-saturated solution, NO^\bullet can be oxidized into NO_2^\bullet or N_2O_4 . It might be supposed that this oxidation does not induce the formation of nitroresorcinol.

iii) This mechanism cannot explain the influence of oxygen in the presence of formate ions.

iv) In air-saturated solution, the formation of 4-nitrosoresorcinol is about 60% inhibited by formate ions (5×10^{-2} M) whereas hydroxyl radicals are more than 90% quenched, as it can be calculated using the rate constants given in Section 4.3.

A reaction of resorcinol with nitrogen monoxide was experimentally excluded and a nitrosation by nitrous acid cannot explain the observed reaction at $\text{pH} > 7$.

On the other hand, the reaction can be related to the formation of nitrogen dioxide, because resorcinol is converted into nitroso derivative only if NO_2^* , and consequently N_2O_3 , can be formed in the solution. The following mechanism in which the nitrosation of resorcinol competes with hydrolysis of N_2O_3 is suggested:



In the absence of formate ions, the influence of NO_2^- concentration on the yield of II can be explained by the competition between reactions 7 and 8. Assuming that the formation of II from NO_2^\cdot is quantitative and that the reaction 7 leads to the disappearance of one molecule of resorcinol, the yield of II is given by:

$$y = \frac{k_8[\text{NO}_2^-]}{k_8[\text{NO}_2^-] + k_7[\text{I}]}$$

$[\text{NO}_2^-](10^{-4} \text{ M})$	5	10	50
y	0.44	0.62	0.89

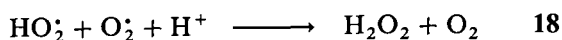
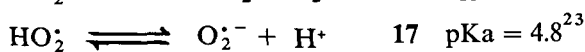
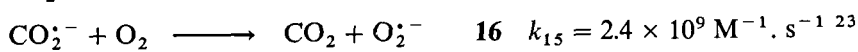
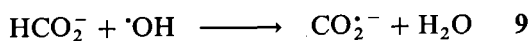
The values of y deduced from the values of k_7 and k_8 given in literature are in very good agreement with the experimental results given in Table 2. It can be deduced that the hydrolysis of N_2O_3 (reaction 14) is not a major pathway compared to the nitrosation (reaction 13). According to this mechanism, no effect of oxygen is expected. However a slight inhibition was observed. It may be attributed to a minor formation of a complex $\text{NO}_2^\cdot \dots$ resorcinol, as it is suggested in the phototransformation induced by excitation of NO_3^- . But in the present work, the effect of oxygen is not important enough to assert this pathway.

In the presence of formate ions $5 \times 10^{-2} \text{ M}$, more than 90% of the $\cdot\text{OH}$ react with these ions; nevertheless, in air-saturated solution, N_2O_3 or N_2O_4 can be formed by

Table 3 Influence of formate ions and ethanol on the formation of 4-nitrosoresorcinol (II) in a solution of resorcinol (5×10^{-4} M) and NaNO_2 (10^{-3} M) irradiated during two hours at 313 nm

		Formation of II (10^{-5} M)
Without $\cdot\text{OH}$ quencher	Aerated	6.1
	Deoxygenated	7.0
Formate ions 5×10^{-2} M	Aerated	2.3
	Deoxygenated	0.27
EtOH 0.17 M	Deoxygenated	0.32

oxidation of $\text{NO}\cdot$ by O_2 or by H_2O_2 resulting from the quenching of $\cdot\text{OH}$:



In deoxygenated solutions, the formation of NO_2^{\cdot} is drastically reduced. From the values of k_7 – k_{10} given in reference 19, the formation of NO_2^{\cdot} can be evaluated to be 21-times lower in the presence of EtOH 0.17 M and 11-times lower in the presence of formate ion 5×10^{-2} M, than in the absence of $\cdot\text{OH}$ quencher. In the case of EtOH, the calculated value is in good agreement with experimental results presented in Table 3. With formate ions, the observed inhibition is about twice higher than the calculated one. This phenomenon can tentatively be explained by a reduction of NO_2^{\cdot} by $\text{CO}_2^{\cdot-}$, that increases the inhibiting effect.

An alternative mechanism should be suggested for the formation of 4-nitrosoresorcinol (II): a reaction of N_2O_4 (or two NO_2^{\cdot}) with resorcinol, since product II can be obtained by excitation of nitrate ions in the presence of resorcinol¹⁸. But this reaction also leads to 4-nitrosoresorcinol, and, in the present work, the formation of this product was not observed. Besides, the formation of N_2O_4 is less probable than the formation of N_2O_3 , because NO_2^{\cdot} is formed from $\text{NO}\cdot$ and the rate constant of formation of N_2O_4 ($k_3 = 4.5 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$) is lower than the rate constant of N_2O_3 ($k_{12} = 1.1 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$). Thus the formation of II from N_2O_4 is most likely a minor pathway.

6 CONCLUSIONS

4-nitrosoresorcinol is the main product formed in the phototransformation of resorcinol induced by excitation of nitrite ions. The specificity of the reaction increases with increasing concentration of NO_2^- .

The quantum yield of the nitrosation is wavelength dependent.

The transformation does not involve a phenoxyl radical, but results from a reaction of a nitrogen oxide (most probably N_2O_3) on resorcinol.

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